Solute Balance Equation

General balance equation. $\frac{\partial u}{\partial t} + \nabla \cdot \vec{j}(u) = \hat{f}(u)$

1) Define unknown to be balanced

- mass/mols of aqueous solute per unit volume of porous medium

$u \equiv \phi \rho_f X = \phi c$

X = mass mo fraction $\left[\frac{M}{M} \text{ or } \frac{N}{N}\right] = [1]$

ρ_f = mass/molar density $\left[\frac{M}{L^3}\right]$ or $\left[\frac{N}{L^3}\right]$

$c = \rho_f X$ = mass/molar concentration $\left[\frac{M}{L^3} \text{ or } \frac{N}{L^3}\right]$

2) Define fluxes

- Advective solute flux due to fluid flow

$\vec{j}_A = \phi \underline{v} c = q c \qquad \left[1 \frac{L}{T} \frac{M}{L^3}\right] = \left[\frac{M}{L^2 T}\right]$ or $\left[\frac{N}{L^2 T}\right]$

- Diffusive solute flux due to concentration gradients

Fick's law: $\vec{j}_D = -\phi \tau D_m \nabla c \qquad \left[1\ 1\ \frac{L^{\cancel{2}}}{T} \frac{1}{\cancel{L}} \frac{M}{L^{\cancel{3}2}} = \frac{M}{L^2 T}\right]$ or $\left[\frac{N}{L^2 T}\right]$

τ = tortuosity of pore space $[1]$

D_m = molecular diffusion coefficient $\left[\frac{L^2}{T}\right]$

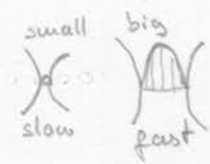
- Mechanical dispersion

Def: Spreading of solutes due to variations in fluid velocity around the average velocity.

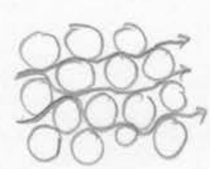
Causes:

a) Velocity variation in single pore (parabolic velocity profile)

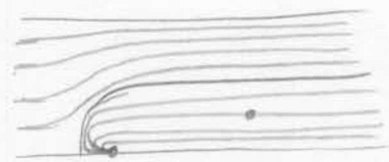
b) Velocity variation between pores of different diameter



c) Variation of the length of the path in different pores



⇒ strongest in direction parallel to velocity
weaker " transverse direction



⇒ Magnitude increases with velocity

⇒ changes orientation with velocity field

Mechanical Dispersion Tensor

$$\boxed{\underline{\underline{D}}_M = (\alpha_L - \alpha_T)\frac{q \otimes q}{|q|} + \alpha_T |q| \underline{\underline{I}}}$$

α_L = longitudinal dispersivity [L]
α_T = transverse dispersivity [L] $\qquad \alpha_T < \alpha_L$
q = volumetric flux $[\frac{L}{T}]$

Outer product. $q \otimes q = q q^T = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} (q_x \; q_y \; q_z) = \begin{pmatrix} q_x^2 & q_x q_y & q_x q_z \\ q_x q_y & q_y^2 & q_y q_z \\ q_x q_z & q_y q_z & q_y^2 \end{pmatrix}$

Spreading due to mechanical dispersion
is only visible in presence of concentration gradient

Dispersive flux $\vec{j}_M = -\underline{\underline{D}}_M(q) \nabla c$

Hydrodynamic dispersion: $\boxed{\underline{\underline{D}}_H = \phi \tau D_m \underline{\underline{I}} + \underline{\underline{D}}_M(q)}$

3) <u>Source term</u>

For now simply a homogeneous reaction

$\hat{f} = \phi k (c - c^{eq})$ $\qquad$ k = reaction rate constant $[\frac{1}{T}]$
c^{eq} = equilibrium concentration $[\frac{M}{L^3}]$ or $[\frac{N}{L^3}]$

Solute balance. $\boxed{\phi \frac{\partial c}{\partial t} + \nabla \cdot [q c - \underline{\underline{D}}_H(q) \nabla c] = \phi k (c - c^{eq})}$